SEASONAL VARIATION OF FLUORIDE, NITRATE AND BORON IN GROUND WATER OF HEBBAL AND CHALLAGHATTA BASINS, BANGALORE, KARNATAKA

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ABSTRACT
Present paper focuses on Physico-chemical characteristics of Hebbal and Challaghatta basins, Bangalore with special reference to fluoride, nitrate and Boron concentration. During the pre-monsoon of 2011, the NO₃⁻ content is as high as (100 mg/l) in 12% of wells having depth of less than 42 feet whereas 88% of samples from wells having depth of more than 799 feet showed < 100 mg/l of NO₃⁻. The higher NO₃⁻ along shallow open wells is therefore attributed to sewage contamination. Pesticides and fertilizers used in agricultural activities are also contributing significant amounts of fluoride to the groundwater regime in Hebbal and Challaghatta aquifers. In the Hebbal and Challaghatta valleys, the industrial applications of boron that apparently could affect the groundwater system are washing powder and agricultural applications of boron-fertilizers and boron-pesticides. The high content of boron in several water sources is signal for restricting the use of washing powder containing boron.

Key word: Seasonal variations, Groundwater, Fluoride, Fluorosis, Nitrate and Boron.

INTRODUCTION
Fluorides are more common in groundwater a surface waters. The main source of fluoride in water is fluoride bearing rocks. The maximum permissible limit for fluoride in drinking water is 1.5mg/l by Bureau of Indian Standards (BIS). When present in higher concentration it causes mottling of teeth, skeletal fluorosis, forward bending of vertebral column, deformation of knee joints and other part of body, and even paralysis (paraplegia, quadriplegia). In the recent, it is documented that the action of fluoride on red blood cells causes a change in the shape of the cells with ultimate destruction, leading to a lower hemoglobin level. The concentrations of fluoride present in groundwater vary considerably over short distance.

In India, majority of fluoride values in water are within 6mg/l. For adults, however the daily intake should not exceed 4mg. Sporadic incidences of high fluoride content in groundwater has been reported from India, West Indies, Sri Lanka, China, Mexico, Italy, Spain, North and South America and Holland. In India, its occurrence in top aquifer system is endemic to many places of Andhra Pradesh, Tamilnadu, Karnataka, Gujarart, Rajasthan, Punjab, Haryana, Bihar and Kerala. It is estimated that fluorides affect about 25 million people in 150 districts in India and peoples are at risk including 6 million children’s suffering from fluorosis because of consumption of higher fluoride. In groundwater, the natural concentration of fluoride depends on the factors such as geological and physico-chemical characteristics of the aquifer, the porosity and acidity of the soil and rocks, temperature, the action of other chemicals and the depth of the well. Present paper focuses on Physico-chemical characteristics of Hebbal and Challaghatta basins, Bangalore with special reference to fluoride, nitrate and Boron concentration.

MATERIALS AND METHODS

Study Area
Thickly populated areas of Hebbal, Challaghatta, Koramangala and Vrishabhavathy valleys witnessing rapid urbanization and Industrialization were selected for this study (Fig. 1). The sewerage network
pattern of these valleys is constituted by a chain of open and closed canals generally flowing from East to West with storage tanks all along ultimately feeding the Arakavathy River, a tributary of River Cauvery. The valleys spread over 77°33’ 09.8″–77°37’10.4″ North Longitude and 13°0’44.3″–13°02’08.6″ East Latitude. The sampling point of groundwater was monitored from nearer the sewerage network (0.5-2km) beside other location. The sampling frequency, year of well establishment (1993-2006), depth (120-800ft.) and yield (1-2.5inch) were recorded at the site itself.

**Geo-Hydrogeology**

Bangalore district and the surrounding areas are entirely underlined by Precambrian granite and gneiss of the Indian Precambrian Shield which are part of the peninsular granitic complex. Migmatite and gneiss are dominant, but there is a zone of granite and granodiorite some 20 km wide trending in a north-northwest direction across the far western part of the district. Minor areas of charnockite occur in the far south western part of the city, and there are some small elongated bodies of amphibolites and schist aligned along a north-south trend through the central part. The Geological and Mineral map of Karnataka and Goa (Anonymous, 1981) show numerous dolerite dykes to the north, west and southwest of Bangalore city. The dominant strike direction is northwest, with a subsidiary concentration of apparently mainly smaller structures having an east north easterly strike. Several thematic maps were prepared to describe the features of Hebbal and Challaghatta valleys viz., Location map of the study area (Fig. 1), Drainage system map (Fig. 2), Geomorphology map, (Fig. 3), Soil map (Fig. 4), and Linament (Structural)/Lithological variations map (Fig. 5).

The aquifer system in the Bangalore urban district is a combination of the shallow weathered zone, which extends to a maximum depth of about 60 m but is commonly less, and there is underlying fresh rock. The hydraulic conductivity of the weathered zone has been enhanced to a small degree, but is still relatively low. The deeper fractured fresh rock part of the aquifer has a very low hydraulic conductivity. Because of this difference in character, they may appear to be independent aquifers, but in the longer term and on a broad scale they will be interconnected. Recharge to the system will be through the shallow weathered zone and from there some water drain into the deeper fractured rock aquifer. Studies indicate that the depth range 30-40 m is clearly the most common to locate water bearing fracture zone. From 40-90 m, there is very little difference in frequency of occurrence, but beyond 90 m the likelihood of intersecting a water-bearing zone decreases rapidly.

**Sampling**

The sampling across Hebbal and Challaghatta valleys included 6 sewage samples, 5 surface water samples (lakes), 8 open wells and 26 bore wells samples selected after assessing the city’s topography, drainage pattern, approach roads, well distribution etc. comprising hand pumps, government water supply lines and private bore wells (Fig. 6).

The samples were collected from each location twice a year, one each during pre and post-monsoon seasons of 2011 and 2012. The excessive standing water in the bore was removed by continuous pumping, prior to the collection of water. Care was taken to avoid excessive withdrawal that may contribute to a mixture of water from different aquifers. Using field water analytical kit (ELICOPE-138) the electrical conductivity and pH were measured at the site. For sample collection, polyethylene bottles of different size with inner cap were used (specification are given at respective sampling method). For each sample, details of location, temperature, odour, colour, turbidity, surrounding environmental conditions etc. were recorded and appropriately labeled, sealed and transported to the laboratory on the same day.

In order to remove all the suspended solids, the samples were filtered through 0.45 µm filter, acidified with 1:1 extra pure grade HNO₃ without disturbing the sample volume, to prevent changes in chemical equilibrium and adsorption of metals to the inner surface of the bottles. pH was adjusted to ≤2 during storage. The samples were stored at 4°C until analysis.
RESULTS AND DISCUSSION

In Hebbal and Challaghatta valleys frequently on a site-specific location, numerous water quality problems have been acknowledged by concerned authorities depending on the nature of contaminant and the nature of surface water (sewerage Network) and groundwater system into which it is introduced. The volume of water in both surface and ground sources has commonly been tended to decline by the enlargement and use of water resources and increased concentration of both natural and anthropogenic contaminants.

The average groundwater temperature during the pre- and post- monsoon seasons of 2011 and 2012 are 26, 26 and 21, 22°C respectively. Marginally higher temperature was recorded during summer and Northeast monsoon (December/January) and a low in the Southwest monsoon (June/July) may be due to the prevalence of cloudy weather as observed by Uyeno, (1966) and Majagi et al., (2011).
Figure 2: Drainage map of Hebbal and Challaghatta.

Figure 3: Geomorphology of Hebbal and Challaghatta.
Figure 4: Soil map of Hebbal and Challaghatta.

Figure 5: Lineament (Structural)/Lithological variations in Hebbal and Challaghatta.
Alternately, in Bangalore city, climate is pleasant and salubrious and devoid of extremes, neither very humid nor very dry. The temperature of the city varies between 28 and 37°C during the hottest months (April/May) and from 16 to 25°C during winter months (December/January). Annual average rainfall over the city is about 850 mm. The high temperature is between 25 to 31°C for surface water and 23 to 31°C for groundwater as revealed by the values recorded during the pre-monsoon of 2011 and 2012. But the lower range is between 19 to 26°C for both surface and groundwater in the post-monsoon of 2011 and 2012. At most locations in Challaghatta valley particularly Sindy Colony, Ulsoor, Domlur, Frazer town, Murgesh playa, Indiranagar and Marathahalli it is above 30°C, but in Hebbal valley during all the seasons and in both the years, the temperature is below 30°C. Twenty-nine percent of samples exhibited pH more than 7.5 during the post-monsoon of 2012 in both the valleys indicating the presence of Carbonates of Ca++ and Mg++. In the study area, the EC during the pre-monsoon of 2011 and 2012 ranged from 130-2250; 126-2062 μS/cm and during post-monsoon of 2011 and 2012, it varied from 102 to 1678 and 118 to 1759 μS/cm respectively. The locations close to sewerage channel showed higher values indicating sewage intrusion into groundwater regime. According to variations in EC and TDS, a majority of Hebbal and Challaghatta valley samples (97, 88, 97 and 73%) fall in ‘high (permissible quality) or light salty’ type whereas around 20% belong to ‘brackish’ category which could be an outcome of over-extraction (Handa, 1969), besides contamination from anthropogenic sources (Jiban Singh et al., 2010 and 2012). Further, on the basis of EC, the groundwater has been classified into: (1) fresh (<1500 μS/cm), (2) brackish (1501–3000 μS/cm) and (3) saline (>3000 μS/cm) types (Saxena et al., 2003). On an average in the area of study 14% of groundwater samples are brackish.

High TDS is accounted by the presence of HCO₃, SO₄, Cl, CaH, MgH, and Na and they elevate the density of water (Nawlakhe et al., 1995). The TDS of precipitation in monsoon of 2011 and 2012 are 14 and 16 mg/l respectively and, the relative values for groundwater during the pre-monsoon of 2011 and 2012 and that of post-monsoon 2011 and 2012, varied from 78 to 1110 and 72 to 1100 and from 62 to 885 mg/l and 60-785 mg/l respectively. Total dissolved solids were highest (74% exceeded the MPL) during
pre-monsoon of 2011, due to evaporation and reduced input and the lowest (71% below the MPL) is during the post-monsoon of 2012, due to an increased input (percolation) from precipitation water. The Chlorides were maximum during summer and minimum during northeast and southwest monsoon. In both Hebbal and Challaghatta valleys, during the pre-monsoon of 2011 and 2012 and post-monsoon of 2011 and 2012, Chlorides varied from 59 to 415, 52 to 360, 33 to 400 and 25 to 315 mg/l respectively. However, the precipitation concentrations during monsoon of 2011 and 2012 are 2 and 4 mg/l respectively. The higher concentration in the present case can definitely be attributed to the industrial activities in the vicinity. In the present case, Cl\(^-\) and HCO\(_3\)^- ions showed a direct relationship with TDS, suggesting that they can be used as effective indicators of contamination.

Consumption of water with higher NO\(_3\)^- causes blue baby or methemoglobinemia in infants and gastric carcinomas, abnormal pain, central nervous system birth defects and diabetes among others. Nitrogen compounds are present in groundwater in the form of nitrate (NO\(_3\)^- ) and nitrite (NO\(_2\)^- ) ions. Nitrates are extremely soluble in water and can move easily through soil into the groundwater. The fertilizers and domestic wastes are the main sources of nitrogen-containing compounds and its concentration may be further affected by complex hydrochemical processes such as nitrification or denitrification (Arnade, 1999; Graniel et al., 1999; Rosen et al., 1999 and Sliva and Williams, 2001). In Bangalore groundwater Nitrate content of about 40% of samples exceeded the Korean Drinking Water Quality Criteria (44.3 mg/l as NO\(_3\)^- ), independent of land-use except forest zones. Organic origin is probably the cause for most of such occurrences, which can be assigned fairly to drainage of water through soil containing domestic and industrial wastes, vegetable and animal matter (Girard and Hillarie Marcel, 1999). Sewage and garbage dump disposals are also responsible for the higher NO\(_3\)^- (Gumtang et al., 1999; Basappa Reddy, 2003 and Owens, 2003).

The NO\(_3\)^- comparatively decreased towards post monsoon. As opinioned by Beck et al., (1985) the seasonal variations of NO\(_3\)^- are caused due to changes in the volume of drainage reaching the water table and not by a change in concentration. In the present case NO\(_3\)^- concentration during the pre-monsoon of 2011 and 2012 varied from 230 to 400; 204 to 283 mg/l (for Surface water) and 38 to 209; 30 to 80 mg/l (for groundwater) respectively. During the post-monsoon of 2011 and 2012, it varied from 201 to 296; 22 to 252 mg/l (for Surface water) and 36 to 56; 19 to 66 mg/l (for groundwater) respectively.

During the pre-monsoon of 2011 and post-monsoon of 2012, the NO\(_3\)^- value of surface and groundwater of NO\(_3\)^- in nearly 96 and 36% of samples exceeded the maximum permissible limit (45 mg/l as per WHO,1994). This included locations of Hebbal and Challaghatta valleys like M.S. Ramaiyanagar, Gokul, Kempapur, Campus of Madras Engineering battalion, Krishna Reddy Layout, Domlur, Mathikere Lake, Habbal Lake, Kalkere Lake, Ulsoor Lake, Bellandur Lake, RMS, 2nd stage, Devinagar, Ganganagar, Anandanagar, Sindy Colony, Ulsoor, Muthyalnagar, GKBK-agriculture College, Anandanagar, Kerena Layout, Chalkere, Kalayanagar, Batanary Road, Frazer town, SBM Colony, Murgesh playla, Divandra palya, Indiranagar, Karnataka Course, 100Ft Road, Krishnamurthynagar, Dickinson Road, Shivajinagar, Near Jayamahal Road and Jeevanahalli recorded higher values. Incessantly, the NO\(_3\)^- values of precipitation during the monsoon season of 2011 and 2012 are 2 and 1 mg/l, whereas more than 50 mg/l of NO\(_3\)^- were found in the groundwater regime of parts of the Hebbal and Challaghatta valleys (e.g. GKBG-agriculture College, Indiranagar, Batanary Road, SBM Colony, Murgesh playla, Devendra playa and Karianna Layout).

The pockets of higher NO\(_3\)^- in the groundwater regime of the study area appear to be related to sewage and agricultural land. A significant correlation between NO\(_3\)^- and Ca\(^++\) and Mg\(^++\) in groundwater strongly indicate that hardness is closely associated with NO\(_3\)^- concentration in Hebbal and Challaghatta valleys. Power and Saikh, (1995); Nolan, (2001); Even et al., (2005) and Reddy et al., (2011), observed that the NO\(_3\)^- concentration is inversely proportional to depth. The data from nearly 34 groundwater samples collected from different locations and depths, during all the seasons of the two years exhibited this trend. During the pre-monsoon of 2011, the NO\(_3\)^- content is as high as (100 mg/l) in12% of wells having depth of less than 42 feet whereas 88% of samples from wells having depth of more than 799 feet showed < 100 mg/l of NO\(_3\)^-. The higher NO\(_3\)^- along shallow open wells is therefore attributed to sewage contamination.
Fluorides are common in ground and surface waters. The main source of fluoride in water is fluoride bearing rocks. The maximum permissible limit for fluoride in drinking water is 1 mg/l (BIS: 10500: 1991). The concentrations of fluoride in groundwater vary considerably over short distance.

**Figure 7: Contour of F⁻ during the Pre-Monsoon of 2011.**

In the study area, during the pre-monsoon of 2011 and 2012, the fluoride concentration ranged from 0.0 to 2.18 and 0.0 to 1.66 mg/l, also, 41 and 3% of sample values are beyond the maximum permissible limit, respectively. During the post-monsoon seasons of 2011 and 2012, the fluoride concentration in groundwater ranged from 0.0 to 0.4 and 0.0 to 0.2 mg/l, (Figs. 7 & 8).

**Figure 8: Contour of F⁻ during the Post-Monsoon of 2012.**
In Hebbal and Challaghatta valleys higher fluorides was observed at Anandanagar, RMS, 2nd stage, Devinagar, Muthyalnagar, GKBK-agriculture College, SBM Colony, Ganganagar, Divandra palya, Kerna Layout and Krishna Reddy Layout etc. On the other hand, once the solubility limit of fluorite (CaF₂) is reached, an inverse relationship appear between fluoride and calcium concentrations, and many studies have found a strong association between high fluoride and soft, alkaline (i.e., NaHCO₃) groundwater with depleted calcium (Bardsen et al., 1996; Conrad et al., 1999; Gupta et al., 1999; Kohut et al., 2001; Earle and Krogh, 2004; Chae et al., 2006a; Dhiman and Keshari, 2006 and Chae et al., 2007). It appears although that the solubility of fluorite (CaF₂) might have reached maximum in Hebbal and Challaghatta valley aquifers. Also an inverse relationship between fluoride and calcium is evident. The source of fluoride contamination in groundwater could be even anthropogenic activities, because even when environmental conditions are held constant in laboratory experiments, the percentage of total leachable fluoride varies widely from one rock type to another (Lirong et al., 2006). Apart from the natural processes which cannot be controlled, huge amount of fluoride are contributed from anthropogenic resources, such as the use of fluoride salts in large number of industries such as steel, aluminum, brick and tiles industries in the present case which often use fluoride. Pesticides and fertilizers used in agricultural activities are also contributing significant amounts of fluoride to the groundwater regime in Hebbal and Challaghatta aquifers.

It is reported that the concentration of fluoride in groundwater does not correlate with the percentage of fluoride-bearing minerals in the geologic substrate in a simple linear fashion (Apambire et al., 1997; Reardon and Wang, 2000; Cronin et al., 2003; Saxena and Ahmed, 2003; Edmunds and Smedley, 2005 and Chae et al., 2007). Although this relationship has been observed in a variety of different high-fluoride environments, it is especially important for areas under land intrusive igneous rocks that have crystallized from highly evolved magmas. Such rocks are not only enriched in fluorine-bearing minerals but also sodium. As a result, the groundwater in contact with these rocks is often soft and calcium-deficient which allows higher fluoride concentrations when equilibrium with fluorite is attained.

The SO₄²⁻ values of precipitation during the monsoon of 2011 and 2012 are the same (2 mg/l), while PO₄ varied marginally (0.0 and 0.01 mg/l). The concentration of SO₄²⁻ in the groundwater during the pre-monsoon of 2011 and 2012 varied from 11 to 386 and 8 to 173 mg/l and during the post-monsoon of 2011 and 2012, it varied from 6 to 219 and 5 to 69 mg/l respectively. During the pre-monsoon of 2011, SO₄²⁻ in 29% of samples from the valleys exceeded the maximum permissible limit (200 mg/l, BIS: 10500:1991), particularly at Pillanaa garden, Kalyannagar, Batanary Road and Indiranagar. But during the post-monsoon of 2012, it is cent percent below the maximum permissible limit in the entire valley. The concentration of PO₄ during the pre-monsoon of 2011 and 2012 varied from 0.0 to 4.46 and 0.0 to 9.64 mg/l and during the post-monsoon of 2011 and 2012 it varied from 0.0 to 2.93 and 0.0 to 8.30 mg/l respectively. During the pre- and post-monsoon of 2011 and 2012, PO₄ in 97 and 82% of groundwater is beyond the maximum permissible limit (0.3 mg/l, BIS: 10500:1991) in various locations.

The natural boron content of ground and surface water is habitually low and is primarily the outcome of leaching from rocks, as dissociated boric acid with some borate ions and soils containing borates and borosilicate. The boron content of surface water can significantly increase as a result of wastewater discharge as borate compounds that are the ingredients of domestic washing agents (ISO, 1990). As a group, the boron-oxygen compounds are sufficiently soluble in water. Concentrations of boron in groundwater throughout the world is reported to range widely from <0.3 to >100 mg/l (Sprague, 1972). In general, its concentrations in southern Europe is high (Italy, Spain) and that of northern Europe is least (Denmark, France, Germany, Netherlands, and United Kingdom). For Italy and Spain, mean boron concentrations range from 0.5 to 1.5 mg/l. Approximately 90% of samples in Denmark, France, and Germany showed concentrations below 0.3, 0.3, and 0.1 mg/l, respectively.

In the study area, the maximum concentrations of boron in groundwater regime during the pre- and post-monsoon of 2011 and pre- and post-monsoon of 2012 are 1.90, 1.20 and 1.84, 0.89 mg/l respectively. Around 44 and 6% of boron concentrations during the pre- and post-monsoon of 2011 are beyond the maximum permissible limit (1 mg/l, BIS: 10500: 1991). Also, 15% samples during the pre-monsoon of
2012 exceeded the permissible limit. However, it is cent percent below the permissible limit during the post-monsoon. Its concentration in precipitation during the monsoon of 2011 and 2012 is nil.

In the Hebbal and Challaghatta valleys, the industrial applications of boron that apparently could affect the groundwater system are washing powder and agricultural applications of boron-fertilizers and boron-pesticides. The high content of boron in several water sources is signal for restricting the use of washing powder containing boron. The locations like, Indiranagar, Tennent 2nd stage, Marathahalli, Devinagar 2nd cross, Ganganagar, HMT Layout, Anandanagar, Muthyalagar, Divandra palya, Kerena Layout, Kalyannagar, Pillanna garden 3rd stage, Batanary Road and Krishna Reddy Layout are the boron rich (>1 mg/l) parts of the study area. Higher concentration of boron presupposes extensive exploitation of groundwater regime in the study area as opinioned by Butterwick et al., (1989).

The boron and Cl concentrations can be used for the comprehension of the provenance of boron in water resources. Chloride is regarded as a conservative element even in geothermal environments. In seawater boron concentrations range between 4.5 and 5 mg/l and B/Cl ratio is 0.0002 mg/l (2 x 10^{-4}). In fossil brines of seawater origin, boron concentrations range between 47.6 and 1379 mg/l and B/Cl ratio range between 0.00056 (5.6 x 10^{-4}) and 0.0099 mg/l (9.9 x 10^{-3}) (Herrmann et al., 1973). In the rain water, boron concentration is approximately 0.01 mg/l while in fresh and uncontaminated surface water it is generally less than 0.05 mg/l with a B/Cl ratio of 0.0013 mg/l (1.3 x 10^{-3}).

**CONCLUSIONS**

Higher temperature in surface and groundwater were recorded during the pre-monsoon and fluctuations in pH were more pronounced during the pre- and post-monsoons of 2011 and 2012 due to an increase the discharge of acidic water via agricultural, domestic and industrials activities in the study area. The EC values for all the seasons of both the years indicated the brackish nature among 14% of groundwater samples. This is outcome of depletion in rainfall and percolation percentage together with increase in the quantum of variable discharges from industrial and residential areas in different parts of Hebbal and Challaghatta valleys. The TDS values are around 18% during the pre-monsoon of 2011, confirming the impact of anthropogenic contamination. During the pre-monsoon, the sewage water in Hebbal and Challaghatta valleys exhibited different colors (*dark blackish, brownish, redish, brown muddish*) and also high density and turbidity. Lakes receiving such water also showed higher color intensity and value, beyond the maximum permissible limit.

During the pre- and post-monsoon of both the years the average value of Chlorides were high, indicating groundwater is contamination from organic sources, like sewage. An inverse relationship between NO₃⁻ and depth of wells, particularly during the pre-monsoon again confirms groundwater contamination from sewage network. During the pre-monsoon of 2011, the F (41%), SO₄²⁻ (29%), PO₄ (97%), total hardness and total alkalinity (97%) were beyond the maximum permissible limit and is attributed to contamination from anthropogenic inputs. High boron concentration occurred at most of the location during the pre-monsoon periods of 2011 and 2012. The surface and groundwater B/Cl ratio is much higher than sea water due to the interaction between industrial effluents and sewerage with groundwater.

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